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(WO/2003/072664) INK COMPOSITIONS CONTAINING LANTHANIDE COMPLEXES

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INK COMPOSITIONS CONTAINING LANTHANIDE COMPLEXES The present invention relates to ink compositions containing lanthanide complexes, a system for marking items with a hidden mark and a method for providing hidden

There is a need for applying hidden marks which can only be revealed under UV exposure on a variety of articles for various reasons.

Thus, security markings are needed on envelopes, checks, bank bills, shares, securities, stamps, identity cards, certificates etc.

Textiles are also furnished with such covert designs which may act as security markings or as special decorations which become visible under UV radiation.

WO 97/10307 discloses a jet ink composition suitable for marking on white or light coloured substrates comprising a fluorescent colorant which is a rare earth metal organic chelate. Those fluorescent colorants are excited by UV radiation in the range of from about 275 nm to about 400 nm and fluoresce in the visible range. However, the luminescence and the quantum yield do not meet the most superior requirements.

It is therefore an object of the present invention to provide an ink composition comprising a colorant which is not visible to the unaided eye but yields a strong luminescence under UV exposure and which composition can be used for all applications on various substrates such as textiles including leather, cellulosic materials, metals, plastic materials, substrates coated with an oligomeric or polymeric matrix and other porous materials.

The invention relates to an ink composition containing (a) a compound of formula I $Lm-Ln3+(Ch)_n$ (1), where L is a lanthanide, Ch is a negatively charged ligand containing at least one UV absorbing double bond, n denotes a number from 1 to 4, in case n is 3, m denotes a number from 1 to 4 and L is a neutral monodentate or polydentate oxygen- or sulfur-containing UV absorbing ligand with the exception of 2, 2'-bipyridyl or, in case n is 4, m denotes

the PC

The compounds of formula I can basically contain any monodentate or polydentate nitrogen-, oxygen- or sulfur- absorbing ligand such as, for example, unsubstituted or substituted pyridine, pyrazine, quinoline, aniline, phenylpyridine, imidazole, benzimidazole, bisimidazole, bisbenzimidazole, pyrimidine, bipyrimidine, naphthyridine, oxazole, bisoxazole, oxazoline, bisoxazoline and substituted derivatives thereof and all relevant (poly-) N-oxides and related ligands.

Preferably L is a nitrogen-containing ligand.

Alkyl groups as substituents R₁ to R₇ can be straight-chain or branched. Examples that may be mentioned are propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, neopentyl, isopentyl, n-hexyl and isohexyl.

Alkoxy groups as substituents R4 to R6 can be, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-but

Examples of C5-C24aryl groups are phenyl, tolyl, mesityl, isityl, diphenyl, naphthyl and anthryl.

Phenyl is preferred.

Heteroaryl group preferably contain 4 or 5 C atoms and one or two heteroatoms selected from O, S and N. E

Aryl groups as substituents R4 to R7 can be, for example, benzyl, 2-phenylethyl, tolylmethyl, mesitylmethyl, chlorophenylmethyl.

Suitable dialkylamino groups are, for example, diethylamino, diisopropylamino, di-n-propylamino, N-methyl-N-pyrrolidino, dimethylamino or pyrrolidino.

Suitable cyclic amino groups are pyrrolidino and piperidino.

Halogen atoms as substituents R4 to R6 are preferably fluorine, chlorine or bromine, but in particular chlorine

Preferred ink compositions according to the invention contain as component (a) a compound of formula 1, a compound of formula V, VI, VII, VIII or IX wherein R₄, R₅ and R₆ are hydrogen, methyl, dimethylamino or py-

Further organic solvents are aliphatic alcohols, glycols, nitroalkanes, dimethylformamide (DMF), dimethylacetamide (DMA), N-methylpyrrolidone (NMP), aliphatic or aromatic ketones, aromatic hydrocarbon esters and aliphatic polyethers.

Glycerol, ethylene glycol and propylene glycol are especially preferred organic solvents.

The ink compositions according to the invention may additionally comprise one or more binder resins (c).

The binder resin serves to immobilize or increase the adhesion of the colorant, particularly on non-porous or example plastic, metallic materials and glassine materials.

Any suitable binder resin can be used. Preferably the binder resin is soluble, dispersible or emulsifiable in the further preferred that the binder resin has sufficient adhesion to the substrate following the dissipation of the

Examples of suitable binder resins include alkyds, acrylic, acrylates, acrylic latexes, epoxy resins, polyvinyl polyurethanes, vinyl resins, polyvinyl acetates, polyvinylalcohol, polyvinylbutyral, PVC, chlorinated rubber, polyethyleneglycol esters of fatty acids, polyalkenes such as polyethylene, polypropylene and polybutylene, methystyrene, copolymers of polyethylene with vinyl acetate, polysulfones, polyesters, polysiloxanes, styrene acrylic copolymers, polyacrylics, polyacrylates such as polymethylacrylate and polymethylmethacrylate, nitrocellulose ethers such as methylcellulose and ethylcellulose, and mixtures thereof.

The compositions according to the invention are well compatible with all conventional aqueous and solvent-based formulations known in the art. Some of these printing formulations are commercially available.

In preferred ink compositions according to the invention the binder resin (c) is selected from the group consisting of polyacrylates, polyurethanes, polyurethane-acrylates, styrene-acrylic copolymers, nitrocellulose and ethylcellulose.

Aqueous ink jet formulations containing polyacrylics, polyacrylates, polyurethanes or polyurethane-acrylates are particularly preferred.

In the compositions according to the present invention the amounts of components (a) and (b) and where applicable (c) are within wide ranges.

Preferred compositions contain 0.01 to 70.0 %, more preferably 0.05 to 30 % and in particular 0.1 to 10.0 %, component (a) and 30.0 to 99.99 %, more preferably 70.0 to 99.95 % and in particular 90.0 to 99.9 %, by weight (b), based on the total amount of components (a) + (b).

High amounts of component (a) are usually well-suited for the ink concentrate in solvent-based applications.

The amount of component (c) depends on the printing application which determines the required viscosity and fixation properties to the substrate. Preferably, the amount of component (c) is 0.5 to 70 %, more preferably in particular 1 to 30 %, by weight, based on the total amount of components (a) + (b) + (c).

Further ingredients which may be present in the ink compositions according to the invention are e. g. natural thickeners, dyes, pigments, optical brighteners, acids, bases and/or salts to adjust the pH to the desired value, or cationic surfactants, antifoaming and antifrosting agents, biocides, bactericides, electrolytes, humectants, and fixing agents.

Especially preferred are compositions according to the invention additionally containing (d) one or more colorants.

Suitable colorants are the well-known pigments and dyes including mixtures of different pigments and dyes.

The ink compositions according to the invention can be prepared by any suitable method known to those of skill in the art. For example, the components of the composition can be combined and mixed in a suitable mixer or blender.

The present invention further provides a system for marking items with a hidden mark which can only be revealed by UV exposure comprising a printing means for printing said mark on said items, wherein said printing means employs the ink composition as described above.

The marking system may additionally include a transport system to carry the items to the printing means. For example, the items can be carried under the print head of an ink jet printer using a conveyor belt.

The present invention further relates to a method for providing a hidden mark on an object, preferably a textile, comprising applying onto said object an ink composition as described above and removing all or substantially all of the ink composition by evaporation or absorption into or onto said object.

The hidden mark can also be hidden into a visible mark, either by overprinting onto a visible mark or by using the ink composition in a formulation, as described in the working examples.

The hidden mark can be made visible by subjecting the object to exciting radiation having a wavelength of from about 300 nm to about 400 nm; the emitted fluorescent radiation is in the visible range, preferably from about 450 nm to about 650 nm, and the emission spectrum contains a sharp emission peak.

The invention can be applied in all customary printing applications like flexographic printing, offset printing, screen printing, transfer printing and textile printing.

A wide variety of substrates can be marked with the fluorescing colorant according to the invention such as natural materials (cotton, leather, silk, polyamide, polyester, mixed fibers, polyacrylonitrile, lycra), cellulosic materials (wood, paper), and plastic materials (polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate); or any other substrate coated with a receiving polymeric or oligomeric matrix, or which can be coated with a polymeric matrix as provided by the binder system (c).

The present invention makes it possible to apply colourless or coloured hidden marks to various colourless, white or dark coloured substrates, which can be revealed under UV exposure. The compositions according to the invention differ from analogous prior art compositions by outstanding luminescence quantum yield, long-lasting luminescence and high luminescence intensity.

The following Examples illustrate the invention.

Ink Composition A: Concentrate of compound XII in 1 g of compound XII (prepared according to Example 1) is dissolved in 99 g of 1,2-propyleneglykol under heating at 100 °C for 1 hour. The clear yellow solution is cooled down and after filtration (clarification) provides the stable Ink Composition A which exhibits an intense red fluorescence under UV light. This concentrate can be further used in either solvent based or aqueous based conventional printing formulations for paper, textile, leather, wood, plastic or other compatible substrates.

Example 1: A colourless aqueous ink-jet ink is prepared by diluting 6 parts by weight of Ink Composition A with 1 part by weight of a standard polyurethane-acrylate aqueous ink-jet ink formulation.

The above described quasi-colourless formulation is printed on white paper, coloured paper, white or coloured textiles and results in a strong red luminescence under UV exposure.

Example 2: A pigmentary yellow aqueous ink-jet ink is prepared by diluting 1 part of Ink Composition A with 1 part of a commercial polyurethane-acrylate pigmentary yellow aqueous ink-jet ink formulation.

The above-described yellow formulation was printed on white paper, coloured paper, white or coloured textiles and results in a strong red luminescence under UV exposure.

Example 3: A pigmentary red aqueous ink-jet ink is prepared by diluting 3 parts of Ink Composition A with 1 part of a commercial polyurethane-acrylate pigmentary red aqueous ink-jet ink formulation. The above-described red ink is printed on white paper, coloured paper, white or coloured textiles and results in a strong red luminescence under UV exposure.

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